INELASTIC COLLISIONS IN H_2O+He SUPERSONIC JETS BY RAMAN SPECTROSCOPY

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Summary

Six supersonic microjets of H_2O+He mixtures with H_2O mole fractions from 1.4% to 33%, have been produced from a 350 micron nozzle at ~90 C.

Jet	$\chi(H_2O)$	χ(He)	P_0 (mbar)
H	34.0	66.0	57.4
K	21.7	78.3	79.8
L	11.5	88.5	120.2
I	6.5	93.5	190.0
J	3.3	96.7	320.0
M	1.4	98.6	309.7

All these jets were checked to be free from H_2O condensation, a must for the quantitative analysis of the collisional kinetics.

The jets were probed by recording the Raman spectra of the Q-branch of the ν_1 symmetric stretching mode at 3657 cm^{-1} at a series of distances *z* along the jet axis.

The primary experimental data are number densities *n(z)* and rotational populations $P_i(z)$ which are then reduced to rotational $T_R(z)$ and translational $T_T(z)$ temperatures. Number densities *n* were obtained by comparing the intensity of the ν_1 Raman band in the jet with that from a static sample at a known number density.

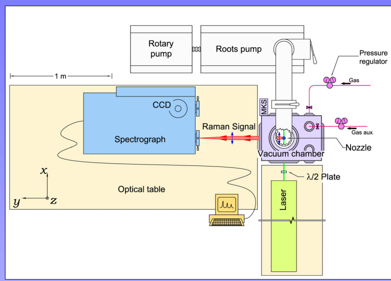
Populations P_i of the lowest rotational energy levels obey a Boltzmann distribution for our stagnation conditions => T_R from simulation of the Raman spectra [1].

Translational temperatures have been obtained from *n(z)* and $T_R(z)$ by conservation of mass, momentum, and energy along the jet [2]. From the analysis of the time evolution of the rotational populations by means of a kinetic Master Equation, we have determined the average rate coefficients, both for H_2O:He and H_2O:H_2O collisions, for the 8 lowest rotational levels of ortho-H_2O, as well as the state-to-state rates for oH_2O:He inelastic collisions at T_t=100 K.

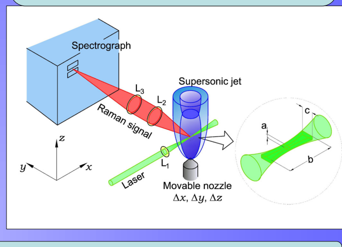
[1] G. Avila et al., J. Molec. Spectrosc. **228**, 38 (2004).

[2] B. Maté et al., J. Chem. Phys. **108**, 2676 (1998).

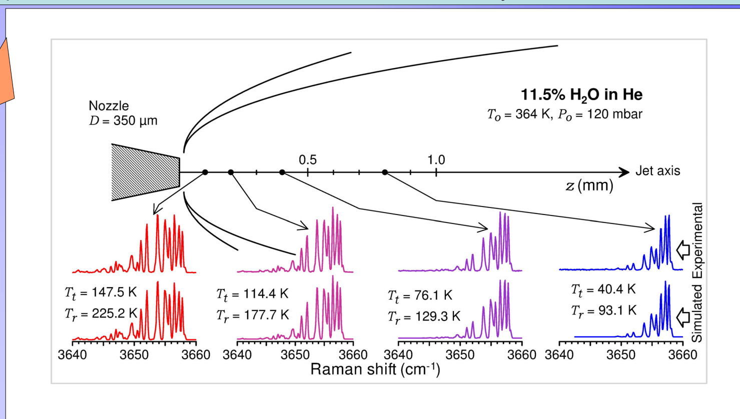
Experimental setup and methodology



-Stable setup (for hours)
-High spatial resolution (few μm)
-High pointing accuracy (~1 μm)



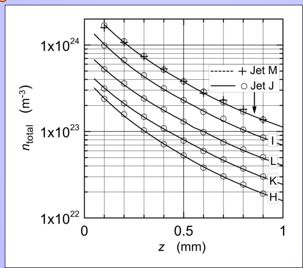
➢Spatial evolution was transformed into time evolution by means of the flow velocity.



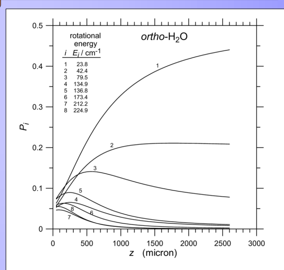
The Master Equation

$$dP_i/dt = \alpha\left(-\sum_{\rho<i} a_{i\rho}h_{i\to\rho} + \sum_{\sigma>i} a_{\sigma i}h_{\sigma\to i}\right)$$
$$+(1-\alpha)\left(-\sum_{\rho<i} a_{i\rho}k_{i\to\rho} + \sum_{\sigma>i} a_{\sigma i}k_{\sigma\to i}\right),$$

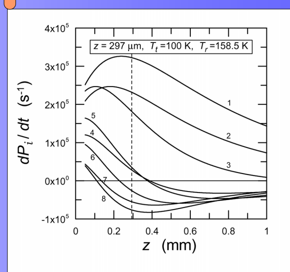
Number densities



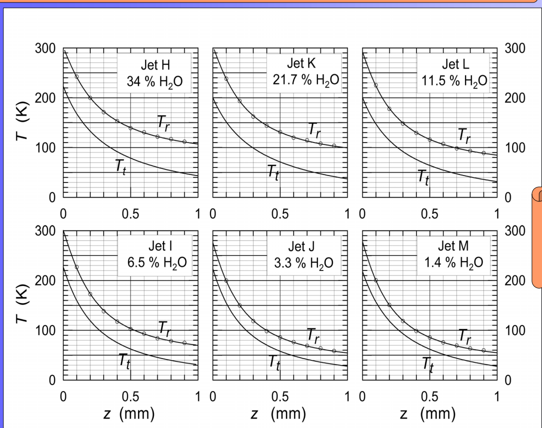
Rotational populations



Time derivatives of Rotational populations



Rotational and translational temperatures



H_2O:He inelastic collisions: State-to-state rate coefficients at 100 K; units of 10^{-14}cm^{3}s^{-1}

A	B	C	D	E	F
$\ell \to i$	$E_\ell - E_i$	$ab-initio^a$	$ab-initio^b$	exptal^c	exptal^d
2 →1	18.6	2025	2451	1548±97	1492±92
3 →1	55.7	1930	2418	1475±92	1472±90
3 →2	37.1	769	745	662±36	517±27
4 →2	92.5	1200	1527	1032±56	1059±56
5 →2	94.4	573	741	493±27	514±27
4 →3	55.4	1180	1492	1270±55	1223±53
5 →3	57.3	1410	1801	1517±66	1476±64
6 →3	93.3	591	719	636±27	589±25
7 →3	132.7	587	760	632±27	623±27
6 →4	38.5	541	664	785±37	779±40
7 →4	77.3	773	825	1121±53	968±49
8 →4	89.9	240	316	348±16	371±19
9 →4	150.5	998	1342	1448±68	1574±80
6 →5	36.6	1335	1610	1717±85	1566±78
8 →5	88.1	1720	2222	2212±109	2162±108
7 →6	38.8	1465	1789	2138±136	1822±123
10 →6	127.0	848	1165	1237±79	1186±80
8 →7	12.7	195	262	363±24	343±24
9 →7	73.3	1245	1554	2326±155	2037±142
10 →7	88.2	419	456	783±52	598±42
12 →7	170.4	686	931	1281±85	1220±85
10 →8	75.5	886	1115	1489±92	1455±95
11 →8	100.5	1770	2287	2975±183	2985±194

C) S. Green et al, Astrophys. J, SS, **85**, 181 (1993)

D) This work, from M. P. Hodges et al PES, J. Chem. Phys. **116**, 1397 (2002)

E), F) This work, experimental

Quantitative analysis

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          ---------------------- dPi/dt  (en 10**3 sec-1) ------------------------
 level i     jet H        Jet K        Jet L        Jet I        Jet J        Jet M
ortho-H2O expt recalc expt recalc expt recalc expt recalc expt recalc expt recalc

    1     180.4 181.6 239.9 238.1 317.9 311.0 431.8 449.2 561.1 561.6 559.3 549.5
oH2O:nH2O       134.7       144.5       130.6       125.4        89.7        40.3
 oH2O:He         46.9        93.6       180.4       323.8       471.9       509.2
exp-rec(%) -1.2 (0.66) +1.8 (0.75) +6.9 (2.17)-17.4 (4.03) -0.5 (0.01) +9.8 (1.75)

    2     133.1 134.2 175.5 173.9 228.7 223.1 308.8 319.5 384.2 388.4 385.6 379.2
                100.8       107.6        96.4        92.4        64.7        29.1
                 33.4        66.3       126.7       227.1       323.7       350.1
          -1.1 (0.83) +1.6 (0.91) +5.6 (2.45)-10.7 (3.46) -4.2 (1.10) +6.4 (1.66)

    3     112.0 114.2 144.3 143.2 179.4 173.2 238.3 239.1 261.0 264.7 267.4 256.6
                 89.4        94.5        82.6        78.5        51.6        23.4
                 24.8        48.7        90.6       160.6       213.1       233.2
          -2.2 (1.96) +1.1 (0.80) +6.2 (3.45) -0.8 (0.33) -3.7 (1.42) +10.8 (4.03)

    4      25.0  26.3  29.1  28.9  28.1  26.3  33.7  28.9   5.0   9.6  10.5   8.2
                 23.0        23.2        18.2        16.4         7.7         3.7
                  3.3         5.7         8.1        12.5         1.9         4.5
            -1.3        +0.2        +1.8        +4.8        -4.6        +2.3

    5      32.4  34.0  37.3  36.7  35.1  33.0  41.4  36.3   0.5   6.8   8.0   7.3
                 29.8        29.5        23.0        20.9         8.9         4.5
                  4.2         7.2        10.0        15.4        -2.1         2.8
            -1.6        +0.6        +2.1        +5.1        -6.3        +0.5

    6      -5.3  -4.4 -11.2 -11.3 -25.1 -25.5 -38.5 -44.6 -84.8 -81.1 -79.8 -80.0
                 -0.2        -2.1        -4.8        -5.7        -8.4        -3.6
                 -4.2        -9.2       -20.7       -38.9       -72.7       -76.4
            -0.9        +0.1        +0.4        +6.1        -3.7        +0.2

    7     -25.3 -25.0 -36.2 -35.9 -53.9 -53.2 -75.7 -80.9 -115.4-114.5 -113.0-111.7
                -16.9       -19.3       -19.5       -19.4       -16.6        -7.3
                 -8.1       -16.6       -33.7       -61.5       -97.9      -104.4
          -0.3 (1.19) -0.3 (0.83) -0.7 (1.30) +5.2 (6.87) -0.9 (0.78) -1.3 (1.15)

    8     -37.2 -36.4 -52.1 -51.4 -75.1 -73.3 -104.4-111.2 -151.3-152.9 -149.1-148.3
                -25.0       -28.2       -27.4       -27.3       -22.7        -9.9
                -11.4       -23.2       -45.9       -83.9      -130.2      -138.4
          -0.8 (2.15) -0.7 (1.34) -1.8 (2.40) +6.8 (6.51) +1.6 (1.06) -0.8 (0.54)
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Average rate coefficients at 100 K units of 10^{-14}cm^{3}s^{-1}

level i	oH_2O:H_2O h_i	oH_2O:He k_i
1	1460±100	262±12
2	1268± 85	217±10
3	1673± 76	249±12
4	1276± 76	162± 8
5	1765±106	227±11
6	1618± 94	188±10
7	1576± 88	167± 8
8	2124±116	209±11

First determination for H_2O:H_2O inelastic collisions

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Inelastic collision rates of *ortho*-H_2O molecules with Helium atoms at 100 K

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An experimental method for the study of inelastic collisions within the vibrational ground state will be reported. The method is based in the production, spectroscopic measurement (Raman), and quantitative analysis of flow data in H_2O+He supersonic jet mixtures. The primary experimental data are number densities and rotational populations which are then reduced to rotational, translational temperatures, and flow velocities. From these data the time evolution of rotational populations of H_2O along the supersonic jets is determined with accuracy up to 1 %. The analysis of time evolution by means of a kinetic Master Equation permit us obtaining the H_2O:H_2O and H_2O:He average rate coefficients associated to each rotational level. Employing the relative values from some *ab-initio* state-to-state rates as starting values, in combination with the H_2O:H_2O self-collision average rates, the experimental state-to-state rate coefficients for H_2O:He inelastic collisions are obtained.

The method is applied here in detail to the state-to-state rates for collisions of *ortho*-H_2O molecules with helium atoms at 100 K. In the experiment the data from six independent H_2O+He supersonic jets with different proportions of helium permit us obtaining the rates for the eight lowest rotational levels of *ortho*-H_2O with accuracy better than 10% for the dominant processes. *Ab-initio* rates from two different H_2O-He potential energy surfaces (PES) [1-3] will be compared with the experiment. Conclusions about the quality of the respective PESs will be discussed.

Broadening coefficients of some rotation lines of *ortho*-H_2O in the THz region, which have been calculated from the inelastic rates reported in this work, will be compared with independent spectroscopic results [4].

References

[1] S. Maluendes, A. D. McLean, and S. Green, J. Chem. Phys. **96**, 8150 (1992).
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[4] M. J. Dick, B. J. Drouin, and J. C. Pearson, Phys. Rev. **A81**, 022706 (2010).